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(54) Title: A LOW-DENSITY AND LOW-POROSITY CEMENTING SLURRY FOR OIL WELLS OR THE LIKE

(57) Abstract: The invention relates to a cement slurry for cementing an oil well or the like, the slurry having a density lying in the range 0.9 g/cm³ to 1.3 g/cm³, and being constituted by a solid fraction and a liquid fraction, having porosity (volume ratio of liquid fraction over solid fraction) lying in the range 38 % to 50 %. The solid fraction is constituted by a mixture of lightweight particles, microcement and optionally portland cement and gypsum. Such cements have remarkable mechanical properties due to their very low porosity in spite of having very low density.



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A LOW-DENSITY AND LOW-POROSITY CEMENTING SLURRY FOR OIL WELLS OR THE LIKE

The present invention relates to drilling techniques for oil wells, gas wells, water wells, geothermal wells, and the like. More precisely, the invention relates to cementing slurries of low density and low porosity.

After an oil well or the like has been drilled, casing or coiled tubing is lowered down the borehole and is cemented over all or part of its height. Cementing serves in particular to eliminate any fluid interchange between the various formation layers that the borehole passes through, preventing gas from rising via the annulus surrounding the casing, or indeed it serves to limit ingress of water into a well in production. Naturally, another main objective of cementing is to consolidate the borehole and to protect the casing.

While it is being prepared and then injected into the well so as to be placed in the zone that is to be cemented, the cementing slurry must present relatively low viscosity and it must have rheological properties that are practically constant. However, once it is in place, an ideal cement would rapidly develop high compression strength so as to enable other work on the well that is being built to start again quickly, and in particular so as to enable drilling to be continued.

The density of the cement must be adjusted so that the pressure at the bottom of the well compensates at least for the pore pressure in the geological formations through which the well passes so as to avoid any risk of eruption. As well as this lower limit on density, there is also an upper limit. This upper limit is that the hydrostatic pressure generated by the column of cement plus the head losses due to the circulation of the fluids being pumped must remain below the fracturing pressure of the rocks in the section being cemented. Certain geological formations are very fragile and require densities close to that of water or even lower.

The risk of eruption diminishes with column height so the density required for compensating pore pressure is then lower. In addition, cementing a large height of column is advantageous since that makes it possible to
5 reduce the number of sections that are cemented. After a section has been cemented, drilling must be restarted at a smaller diameter, so having a large number of sections requires a hole to be drilled near the surface that is of large diameter, thereby giving rise to excess cost due to
10 the large volume of rock to be drilled and due to the large weight of steel required for the sections of casing, given their large diameters.

All of those factors favor the use of cement slurries of very low density.

15 The cement slurries in the most widespread use have densities of about 1900 kg/m^3 , which is about twice the density desired for certain deposits. To lighten them, the simplest technique is to increase the quantity of water while adding stabilizing additives (known as
20 "extenders") to the slurry for the purpose of avoiding particles settling and/or free water forming at the surface of the slurry. Manifestly, that technique cannot get down to a density close to 1000 kg/m^3 . Furthermore, hardened cements formed from such slurries have greatly
25 reduced compression strength, a high degree of permeability, and poor adhesive capacity. For these reasons, that technique cannot be used to go below densities of about 1300 kg/m^3 while still conserving good isolation between geological layers and providing
30 sufficient reinforcement for the casing.

Another technique consists in lightening the cement slurry by injecting gas into it (generally air or nitrogen) before it sets. The quantity of air or nitrogen added is such as to reach the required density.
35 It can be such as to form a cement foam. That technique provides performance that is a little better than the preceding technique since the density of gas is lower

than that of water, so less needs to be added.

Nevertheless, in oil industry applications density remains limited in practice to densities greater than 1100 kg/m³, even when starting with slurries that have already been lightened with water. Above a certain "quality of foam", i.e. a certain ratio of gas volume to volume of the foamed slurry, the stability of the foam falls off very quickly, the compression strength of the foam after it has set becomes too low, and its permeability becomes too high, thereby compromising durability in a hot aqueous medium which includes ions that are aggressive to a greater or lesser extent for cement.

An object of the present invention is to provide cementing slurries that are more particularly adapted to cementing oil wells or the like, having both low density and low porosity, and that are obtained without introducing gas.

According to the invention, this object is achieved by a cement slurry for cementing an oil well or the like, the slurry having a density lying in the range 0.9 g/cm³ to 1.3 g/cm³, in particular in the range 0.9 g/cm³ to 1.1 g/cm³, and being constituted by a solid fraction and a liquid fraction, having porosity (volume ratio of liquid fraction over solid fraction) lying in the range 38% to 50%, and preferably less than 45%.

The solid fraction is preferably constituted by a mixture comprising:

- 60% to 90% (by volume) of lightweight particles having a mean size lying in the range 20 microns (µm) to 350 µm;
- 10% to 30% (by volume) of micro-cement having a mean particle diameter lying in the range 0.5 µm to 5 µm;
- 0 to 20% (by volume) of Portland cement, having particles with a mean diameter lying in the range 20 µm to 50 µm; and
- 0 to 30% (by volume) of gypsum.

The low porosities achieved make it possible to optimize mechanical properties and permeability. By presenting mechanical properties that are much better than those of conventional lightened systems, and
5 permeabilities that are lower, the leakproofing and adhesion properties of ultralightweight cement and the resistance of such formulations to chemical attack are thus much better than with the systems presently in use for low densities, even though the invention makes it
10 possible to reach densities that are exceptionally low, and in particular that are lower than the density of water. In addition, slurries of the invention do not require gas, thus making it possible to avoid the logistics that would otherwise be required for
15 manufacturing foamed cements.

The method of the invention is characterized in that particulate additives are incorporated in the cement slurry, such that in combination with one another and with the other particulate components of the slurry, and
20 in particular with the particles of micro-cement (or comparable hydraulic binder), they give rise to a grain-size distribution that significantly alters the properties of the slurry. The said particulate additives are organic or inorganic and they are selected for their
25 low density.

The low density is obtained by combining lightweight particles and cement (or a comparable hydraulic binder). Nevertheless, rheological and mechanical properties will only be satisfactory if the size of the particles and the
30 volume distribution thereof is selected in such a manner as to maximize the compactness of the solid mixture.

For a solid mixture having two components (the lightweight particles and the micro-cement), this maximum compactness is generally obtained for a volume ratio of
35 lightweight particles to micro-cement lying in the range 70:30 to 85:15, and preferably in the range 75:25 to 80:20, for lightweight particles selected to be of a size

that is at least 100 times approximately the size of the particles of micro-cement, i.e. in general, particles that are greater than 100 μm in size. These values can vary, in particular as a function of the greater or
5 lesser dispersion in the grain-size distribution of the lightweight particles. Particles having a mean size greater than 20 microns can also be used, but performance is not so good. Particles greater than 350 microns are generally not used because of the narrow size of the
10 annular gaps to be cemented.

Mixtures having three or more components are preferred since they make it possible to obtain greater compactness if the mean sizes of the various components are significantly different. For example, it is possible
15 to use a mixture of lightweight particles having a mean size of 150 microns, lightweight particles having a mean size of 30 microns, and micro-cement, at a volume ratio lying close to 55:35:10, or departing a little from these optimum proportions, the mixture being constituted by 50%
20 to 60% (by volume) of the first lightweight particles of mean diameter lying in the range 100 μm to 400 μm , 30% to 45% of the second lightweight particles of mean diameter lying in the range 20 μm to 40 μm , and 5% to 20% of micro-cement. Depending on the application, the fraction
25 of lightweight particles of intermediate size can be replaced by Portland cement of ordinary size, in particular class G Portland cement.

The term "micro-cement" is used in the invention to designate any hydraulic binder made up of particles of
30 mean size of about 3 μm and including no, or at least no significant number of, particles of size greater than 10 μm . They have a specific surface area per unit weight as determined by the air permeability test that is generally about 0.8 m^2/g .

35 The micro-cement can essentially be constituted by Portland cement, in particular a class G Portland cement typically comprising about 65% lime, 25% silica, 4%

alumina, 4% iron oxides, and less than 1% manganese oxide, or equally well by a mixture of Portland micro-cement with microslag, i.e. a mixture making use essentially of compositions made from clinker comprising
5 45% lime, 30% silica, 10% alumina, 1% iron oxides and 5% to 6% manganese oxide (only the principal oxides are mentioned here; and these concentrations can naturally vary slightly as a function of the supplier). For very low temperature applications ($< 30^{\circ}\text{C}$), Portland micro-
10 cement is preferable over a mixture of micro-cement and slag because of its reactivity. If setting at right angles is required, plaster (gypsum) can be used for all or some of the middle-sized particles.

The lightweight particles typically have density of
15 less than 2 g/cm^3 , and generally less than 0.8 g/cm^3 . By way of example, it is possible to use hollow microspheres, in particular of silico-aluminate, known as cenospheres, a residue that is obtained from burning coal and having a mean diameter of about $150 \mu\text{m}$. It is also
20 possible to use synthetic materials such as hollow glass beads, and more particularly preferred are beads of sodium-calcium-borosilicate glass presenting high compression strength or indeed microspheres of a ceramic, e.g. of the silica-alumina type. These lightweight
25 particles can also be particles of a plastics material such as beads of polypropylene.

In general, the density of the slurry is adjusted essentially as a function of which lightweight particles are chosen, but it is also possible to vary the ratio of
30 water to solid (keeping it in the range 38% to 50% by volume), the quantity of micro-cement or of comparable hydraulic binder (in the range 10% to 30%), and adding Portland cement of ordinary size as a replacement for a portion of the lightweight particles.

35 Naturally, the slurry can also include one or more additives of types such as: dispersants; antifreeze; water retainers; cement setting accelerators or

retarders; and/or foam stabilizers, which additives are usually added to the liquid phase, or where appropriate incorporated in the solid phase.

Formulations made in accordance with the invention
5 have mechanical properties that are significantly better than those of foamed cements having the same density. Compression strengths are very high and porosities very low. As a result, permeabilities are smaller by several orders of magnitude than those of same-density foamed
10 cements, thereby conferring remarkable properties of hardness on such systems.

The method of the invention considerably simplifies the cementing operation, since it avoids any need for logistics of the kind required for foaming.

15 Slurries prepared in accordance with the invention also have the advantage of enabling all of the characteristics of the slurry (rheology, setting time, compression strength, ...) to be determined in advance for the slurry as placed in the well, unlike foamed
20 slurries where certain parameters can be measured on the slurry only prior to the introduction of gas (setting time).

The following examples illustrate the invention without limiting its scope.

25

EXAMPLE 1

Low-density and low-porosity slurries can be obtained from mixtures of particles of two or three (or even more) different sizes, so long as the packing volume
30 fraction (PVF) is optimized.

The properties of three slurries prepared in accordance with the invention are described and compared with those of a conventional low-density extended slurry and of a foamed system:

35 Slurry A: A mixture of powders was prepared. It comprised 55% by volume of hollow spheres taken from cenospheres having an average size of 150 microns

(specific gravity 0.75); 35% by volume of glass microspheres having an average size of 30 microns; and 10% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

5 The microspheres used are sold by 3MTM under the name Scotchlite S60/10,000; such microspheres have a density of 0.6 g/cm³ and a grain-size distribution such that 10% of the particles (by volume) have a size of less than 15 μ m, 50% less than 30 μ m, and 90% less than 70 μ m;
10 these particles were selected in particular because of their high compression strength (90% of the particles withstand isostatic compression of 68.9 MPa or 10,000 psi).

 Water and the following additives were mixed with
15 this powder so as to ensure that the volume percentage of liquid in the slurry was 42%: water retainer based on 2-acrylamido 2-methylpropane sulfonic acid (AMPS) at 0.2% (percent by weight of powder, i.e. all of the solid particles taken together (micro-cement, microspheres and
20 cenospheres for this slurry A)); an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.07 gallons per bag of powder. It should be observed that a bag of powder is defined by analogy with bags of cement as being
25 a bag containing 45.359 kg of mixture, in other words 1 gpb = 0.03834 liters (/) of additive per kg of mixture.

Slurry B: A mixture of powders was prepared. It comprised 78% by volume of hollow spheres obtained from cenospheres having a mean size of 150 microns and a
30 density of 0.63 g/cm³, and 22% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

 Water and the following additives were mixed with the powder so that the volume percentage of liquid in the
35 slurry was 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based

on polynaphthalene sulfonate at 0.1 gallons per bag of powder.

5 Slurry C: A mixture of powders was prepared. It comprised 78% by volume of Scotchlite glass microspheres having a mean size of 30 microns, and 22% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

10 Water and the following additives were mixed with said powder so that the volume percentage of liquid in the slurry was 45%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.145 gallons per bag of powder.

15 Slurry D: A mixture of powders was prepared. It comprised 78.4% by volume of hollow spheres derived from cenospheres having a mean size of 150 microns (density 0.72 g/cm³) and 21.6% by volume of glass G Portland cement.

20 Water and the following additive were mixed with said powder so that the volume percentage of liquid in the slurry was 57%: an antifoaming agent at 0.03 gallons per bag of powder.

25 Slurry E: A conventional slurry of density 1900 kg/cm³ was prepared based on a class G Portland cement.

The slurry was foamed with a quantity of foam of 50% so as to obtain a slurry whose final density was 950 kg/m³.

Slurry	A	B	C	D	E
Density	924 (7.7)	1068 (8.9)	1056 (8.8)	1130 (9.4)	950 (7.9)
Porosity	42%	42%	45%	57%	78%*
PV	87	68	65		
Ty	3.7 (7.7)	8.6 (18)	3.4 (7.2)		
CS	11.7 (1700)	19.3 (2800)	14.5 (2100)	2.48 (360)	4.62 (670)

The densities are expressed in kg/m³ (and in pounds per gallon in parentheses). Rheology is expressed by a flow threshold Ty in Pascals (and in pounds per 100 square feet in parentheses), and by plastic viscosity in mPa.s or centipoise, using the Bingham fluid model. These parameters were determined at ambient temperature. CS means compression strength after 24 hours for cement set at 60°C (140°F) at a pressure of 6.9 MPa (1000 psi), and it is expressed in Mpa (and in pounds per square foot in parentheses).

* In this case, porosity was calculated as volume of gas + water over total volume of the slurry.

It can be seen that for the slurries prepared in accordance with the invention, compression strength is particularly high for densities that are so low and that these slurries present excellent rheology in spite of their low porosity.

EXAMPLE 2

For slurries having a density greater than 8 pounds per gallon (ppg), a portion of the lightweight particles can be substituted by class G cement.

Slurry A: A mixture of powders was prepared. It comprised 55% by volume hollow spheres derived from cenospheres having a mean size of 150 microns, 35% by

volume of Scotchlite glass microspheres having a mean size of 30 microns, and 10% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

5 Water and the following additives were mixed with the powder so that the volume percentage of the liquid in the slurry was 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based
10 on polynaphthalene sulfonate at 0.07 gallons per bag of powder.

Slurry B: A mixture of powders was prepared. It comprised 55% by volume of hollow spheres derived from cenospheres having a mean size of 150 microns, 25% by
15 volume of Scotchlite glass microspheres having a mean size of 30 microns, 10% by volume of a class G Portland cement, and 10% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

 Water and the following additives were mixed with
20 the powder so as obtain a volume percentage of liquid in the slurry of 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based
25 on polynaphthalene sulfonate at 0.01 gallons per bag of powder.

Slurry C: A mixture of powders was prepared. It comprised 55% by volume of hollow spheres derived from cenospheres having a mean size of 150 microns, 20% by
30 volume of Scotchlite glass microspheres having a mean size of 30 microns, 15% by volume of a class G Portland cement, and 10% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

 Water and the following additives were mixed with
35 the powder so that the volume percentage of liquid in the slurry was 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based

on polynaphthalene sulfonate at 0.01 gallons per bag of powder.

Slurry D: A mixture of powders was prepared. It comprised 55% by volume of hollow spheres derived from cenospheres having a mean size of 150 microns, 15% by volume of Scotchlite glass microspheres having a mean size of 30 microns, 20% by volume of a class G Portland cement, and 10% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

Water and the following additives were mixed with the powder so as to obtain a volume percentage of liquid in the slurry of 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.01 gallons per bag of powder.

Densities are expressed in kg/m^3 (and in pounds per gallon in parentheses). Rheology is expressed by the flow threshold T_y in Pascals (and in pounds per 100 square feet in parentheses), and by plastic viscosity PV in $\text{mPa}\cdot\text{s}$ or centipoise, using the Bingham fluid model. These parameters were determined at ambient temperature. CS stands for compression strength after 24 hours and after 48 hours for cement setting at 60°C at a pressure of 6.9 MPa (1000 psi), expressed in MPa (and in pounds per square foot in parentheses).

Slurry	A	B	C	D
Density	924 (7.7)	1068 (8.9)	1140 (9.5)	1218 (10.15)
Porosity	42%	42%	42%	42%
PV	87	90	100	109
Ty	7.7	8.8	9.0	11.2
CS (24 h)	7.58 (1100)	18.3 (2650)	19.7 (2850)	20.7 (3000)
CS (48 h)	9.0 (1300)	19.0 (2750)	29.7 (4300)	28.3 (4100)

Adding Portland cement as a portion of the "medium-sized" particles makes it possible to cover the entire range of densities from 8 ppg to 11 ppg and significantly improves compression strength. This addition does not disturb the good rheological properties in any way.

EXAMPLE 3

For slurries having a density greater than 8 ppg, a portion of the lightweight particles can be substituted by micro-cement or by a mixture of micro-cement and slag.

Slurry A: A mixture of powders was prepared. It comprised 55% by volume hollow spheres derived from cenospheres having a mean size of 150 microns, 30% by volume of Scotchlite glass microspheres having a mean size of 30 microns, and 15% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

Water and the following additives were mixed with the powder so that the volume percentage of the liquid in the slurry was 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.07 gallons per bag of powder.

Slurry B: A mixture of powders was prepared. It comprised 55% by volume hollow spheres derived from cenospheres having a mean size of 150 microns, 25% by volume of Scotchlite glass microspheres having a mean size of 30 microns, and 20% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

Water and the following additives were mixed with the powder so that the volume percentage of the liquid in the slurry was 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.07 gallons per bag of powder.

Slurry	A	B
Density	990 (8.25)	1056 (8.8)
Porosity	42%	42%
CS (24 h)	11.2 (1630)	21.4 (3100)
CS (48 h)	11.7 (1700)	22.1 (3200)

Densities are expressed in kg/m³ (and in pounds per gallon in parentheses). CS means compression strength after 24 hours and 48 hours for cement set at 60°C under a pressure of 6.9 MPa (1000 psi), expressed in MPa (and in pounds per square foot in parentheses).

Increasing the content of micro-cement and slag mixture gives rise to exceptional compression strength performance at 9 ppg.

EXAMPLE 4

Depending on the desired mechanical properties (flexibility, ability to withstand high pressures), various lightweight particles can be used so long as the PVF is optimized.

Slurry A: A mixture of powders was prepared. It comprised 55% by volume hollow spheres derived from cenospheres having a mean size of 150 microns, 30% by volume of hollow spheres derived from cenospheres having a mean size of 45 microns, and 15% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

Water and the following additives were mixed with the powder so that the volume percentage of the liquid in the slurry was 42%: water retainer based on AMPS polymer at 0.2% by weight of powder; an antifoaming agent at 0.03 gallons per bag of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.07 gallons per bag of powder.

Slurry B: A mixture of powders was prepared. It comprised 55% by volume of particles of polypropylene having a means size of 300 microns, 30% by volume of Scotchlite glass microspheres having a mean size of 30 microns, and 15% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

Water and the following additives were mixed with the powder so that the volume percentage of the liquid in the slurry was 42%: a retarder based on purified lignosulfonates at 0.22% by weight of powder; a water retainer based on AMPS polymer at 0.2% by weight of powder; and a super-plasticizer based on polynaphthalene sulfonate at 0.05 gallons per bag of powder.

Slurry	A	B
Density	990 (8.25)	1068 (8.9)
Porosity	42%	42%
PV	93	116
Ty	20	9.3
CS (24 h)	18.3 (2640)	10.3 (1500) *
CS (48 h)	18.7 (2700)	22.1 (3200) *

Densities are expressed in kg/m³ (and in pounds per gallon in parentheses). Rheology is expressed by the flow threshold T_y in Pascals (and in pounds per 100 square feet in parentheses), and by plastic viscosity PV in mPa.s or centipoises, using the Bingham fluid model. These parameters were determined at ambient temperature. CS means compression strength at 24 hours and at 48 hours from the cement setting at 60°C under 6.9 MPa (1000 psi), expressed in MPa (and in pounds per square foot in parentheses).

* Compression strength at 24 hours for cement set at 104°C (220°F) under a pressure of 20.7 MPa (3000 psi), expressed in MPa and in psi in parentheses.

15

EXAMPLE 5

For low temperature applications, the mixture of micro-cement and slag can be substituted by pure micro-cement, or plaster can be added to replace the medium-sized particles.

20

We have compared a formulation of the invention with a foamed plaster formulation.

Slurry A: A mixture of powders was prepared. It comprised 42.7% by volume of hollow spheres derived from cenospheres having a mean size of 150 microns, 20% by volume of hollow spheres derived from cenospheres having a mean size of 45 microns, 27.3% by volume of gypsum, and 10% by volume of a mixture of Portland micro-cement and slag having a mean size of about 3 microns.

Water and the following additives were mixed with the powder so that the volume percentage of liquid in the slurry was 42%: retarder based on purified lignosulfonates at 0.05 gallons per bag of powder; a water retainer of the example at 0.04 gallons per bag of powder; and an antifoaming agent at 0.03 gallons per bag of powder.

35

Slurry B (reference): This slurry corresponds to the prior art. A mixture of powders was prepared. It comprised 40% by volume of class G cement and 60% by volume of plaster. Water and additives were mixed with the powder so that the density of the slurry was 1900 kg/m³ (15.8 ppg).

To foam this slurry, entirely conventional wetting agents were added: D138 and F052.1 in a 1:1 ratio. The quantity added depends on foam quality. It was adjusted so as to obtain a slurry having a density of 1320 kg/m³ (11 pounds per gallon).

Densities		1320 (11)	1218 (10.15)
Slurry A (of the invention)	Q		0
	PV		112
	Ty		6.7
	CS (at 12 hours for cement set at 4°C under 6.9 MPa)		2.41 (350)
	CS (at 24 hours for cement set at 25°C under 6.9 MPa)		14.8 (2150)
Slurry B (reference)	Q	30%	
	CS (at 24 hours for cement set at 18°C under atmospheric pressure)	2.96 (430)	
	CS (at 48 hours for cement set at 18°C under atmospheric pressure)	4.55 (660)	

Densities are expressed in kg/m³ (and in pounds per gallon in parentheses). Rheology is expressed by the flow threshold Ty in Pascals (and in pounds per 100 square feet in parentheses), and by plastic viscosity PV in mPa.s or centipoises, using the Bingham fluid model.

These parameters were determined at ambient temperature. CS stands for compression strength under conditions stated in the table, expressed in MPa (and in pounds per square foot in parentheses).

CLAIMS

1/ A cement slurry for cementing an oil well or the like, the slurry having a density lying in the range 0.9 g/cm³ to 1.3 g/cm³, and being constituted by a solid fraction
5 and a liquid fraction, having porosity (volume ratio of liquid fraction over solid fraction) lying in the range 38% to 50%, said solid fraction comprising :

- 10 • 60% to 90% (by volume) of lightweight particles having a mean size lying in the range 20 microns (µm) to 350 µm;
- 10% to 30% (by volume) of micro-cement having a mean particle diameter lying in the range 0.5 µm to 5 µm;
- 0 to 20% (by volume) of Portland cement, having particles with a mean diameter lying in the range 20 µm
15 to 50 µm; and
- 0 to 30% (by volume) of gypsum.

2/ A cement slurry according to claim 1, characterized by porosity of less than 45%.

20 3/ A cement slurry according to any preceding claim, characterized in that said lightweight particles have a density of less than 2 g/cm³, and preferably less than 0.8 g/cm³.

25 4/ A cement slurry according to claim 3, characterized in that said lightweight particles are selected from hollow microspheres, in particular silico-aluminate microspheres or cenospheres, synthetic materials such as hollow glass
30 beads, and more particularly beads of sodium-calcium-borosilicate glass, ceramic microspheres, e.g. of the silica-alumina type, or beads of plastics material such as polypropylene beads.

35 5/ A cement slurry according to any preceding claim, characterized in that the slurry has one or more additives of the following types: dispersants,

antifreeze, water retainers, cement setting accelerators or retarders, and foam stabilizers.

- 5 6/ A cement slurry according to any preceding claim, characterized in that the solid fraction of the slurry is constituted by lightweight particles of diameter lying in the range 100 μm to 350 μm and by particles of micro-cement, with the ratio of lightweight particles to micro-cement lying in the range 70:30 to 85:15.
- 10 7/ A cement slurry according to any one of claims 1 to 6, characterized in that the solid fraction of the mixture is constituted by 50% to 60% (by volume) of first lightweight particles having a mean diameter lying in the
- 15 range 100 μm to 400 μm , by 30% to 45% of second lightweight particles of mean diameter lying in the range 20 μm to 40 μm , and by 5% to 20% of micro-cement.
- 20 8/ Use of the slurry according to any preceding claim in cementing oil, gas, or similar wells.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/06459

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C04B28/02 E21B33/13 C04B28/08 //(C04B28/02,7:02,22:14,38:08),C04B201:20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C04B E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 00 29351 A (SOFITECH NV ; SCHLUMBERGER CA LTD (CA); SCHLUMBERGER CIE DOWELL (FR) 25 May 2000 (2000-05-25) page 3, line 33 -page 4, line 14 ----	1-8
Y	US 3 804 058 A (MESSENGER J) 16 April 1974 (1974-04-16) claims; table II ----	1,3-6,8
Y	US 5 571 318 A (GRIFFITH JAMES E ET AL) 5 November 1996 (1996-11-05) column 8, line 33 - line 64; example 2 ----	1,3-6,8
A	GB 2 027 687 A (STANDARD OIL CO) 27 February 1980 (1980-02-27) page 3, line 38 -page 4, line 2; claims ----- -/--	1,3-8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

6 November 2000

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INTERNATIONAL SEARCH REPORT

Intern: al Application No
PCT/EP 00/06459

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 814 067 A (SOFITECH NV) 29 December 1997 (1997-12-29) page 2, line 28 - line 52; claims -----</p>	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern: al Application No

PCT/EP 00/06459

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0029351 A	25-05-2000	AU 1241999 A	05-06-2000
US 3804058 A	16-04-1974	US 3902911 A	02-09-1975
US 5571318 A	05-11-1996	NONE	
GB 2027687 A	27-02-1980	US 4252193 A	24-02-1981
		AU 524956 B	14-10-1982
		AU 4961879 A	14-02-1980
		BR 7905034 A	22-04-1980
		CA 1126300 A	22-06-1982
		DE 2932203 A	21-02-1980
		EG 14041 A	30-09-1983
		FR 2439169 A	16-05-1980
		IT 1120490 B	26-03-1986
		MX 152715 A	21-10-1985
		NL 7906030 A	12-02-1980
		NO 792587 A, B,	11-02-1980
		RO 78647 A	24-03-1982
		US 4305758 A	15-12-1981
EP 0814067 A	29-12-1997	FR 2749844 A	19-12-1997
		CA 2207885 A	18-12-1997
		NO 972799 A	19-12-1997
		US 6060535 A	09-05-2000